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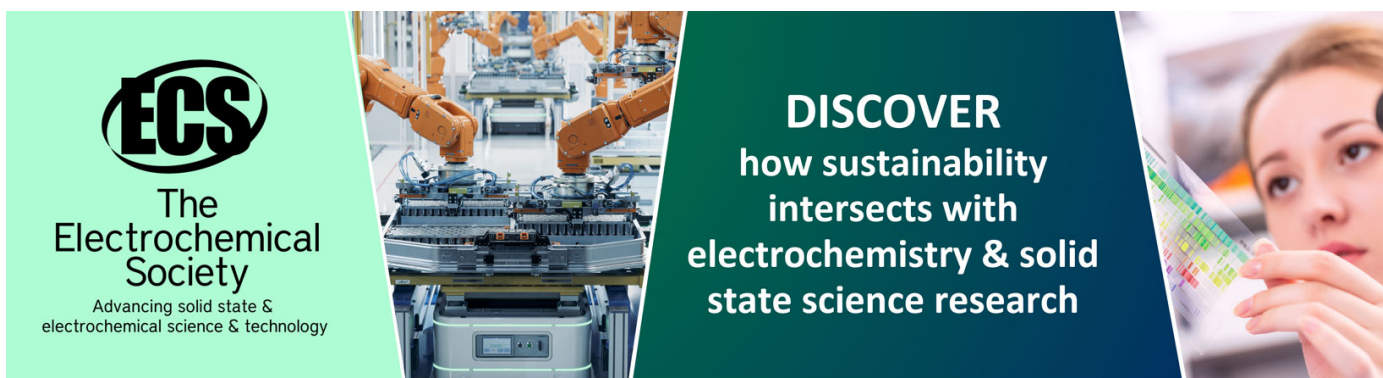
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Theoretical modeling of the hybrid membrane-gas hydrate crystallisation process for xenon recovery

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Abstract. A mathematical model of the hybrid membrane-gas hydrate crystallisation for xenon (Xe) recovery from binary gas mixtures approximated to natural gas composition and normalised by 100% is considered. The first gas mixture is CO₂ (97.09 vol.%) and Xe (2.91 vol.%). The second gas mixture is H₂S (97.09 vol.%) and Xe (2.91 vol.%). The third gas mixture is CH₄ (99.84 vol.%) and Xe (0.16 vol.%). Poly(dimethylsiloxane) and Cellulose triacetate membranes are used. The process at the gas hydrate mixture dissociation pressures and the gas hydrate formation temperature is 275.15 K. The dependences of the gas hydrate, the membrane, the hybrid membrane-gas hydrate Xe recoveries through the membranes versus gas mixture withdrawn are obtained. Xe has the good gas hydrate-forming properties and will be the most effective concentration in the gas hydrate phase. For the most efficient Xe recovery in the membrane-gas hydrate module must not be impurities with the gas hydrate dissociation pressure and permeability through the membrane close to Xe. It is shown that the largest Xe recovery is 20.08 in CH₄ (99.84 vol.%) and Xe (0.16 vol.%) gas mixture. Thus, the efficiently Xe recovery from the main natural gas component – CH₄ by the hybrid membrane-gas hydrate crystallisation is possible.

1. Introduction

Xenon (Xe) is used in many lines of industries, among them: chemical [1–3], medical [4,5], space [6,7], and automotive [8,9]. Xe concentration in the air is 0.087 ppm [10], and its production is highly energy-consuming. Xe concentration in natural gas is 0.15 vol.% (and possibly more) [11], which is four orders of magnitude greater than in the air. Thereby, Xe recovery from natural gas is a priority.

At present, when literature data are studying, there is no industrial production of Xe recovery from natural gas. Natural gas consists of hydrocarbon (60 - 95 vol.%) and other gases [12]. The gas hydrate dissociation pressures forming natural gas are very different ($P_{dis}(\text{CH}_4) > P_{dis}(\text{CO}_2) > P_{dis}(\text{C}_2\text{H}_6) > P_{dis}(\text{C}_3\text{H}_8) > P_{dis}(\text{Xe}) \approx P_{dis}(\text{H}_2\text{S})$ etc. [13]). As seen, Xe and H₂S gas hydrate dissociation pressures are the smallest and almost equal. Consequently, their separation from the main natural gas component (CH₄) by the gas hydrate crystallisation will be effective. For the further Xe and hydrogen sulphide (H₂S) separation, the most energy efficient process is the membrane gas separation [14,15], since Xe permeability through the elastomeric membranes is two orders of magnitude lower than for H₂S [16,17]. For increase Xe recovery from gas mixtures that are close to natural gas composition, it is necessary to realise a hybrid process, i.e., to realise the membrane separation and the gas hydrate crystallisation in one mass-exchange apparatus.

Xe is low-permeable component, that is, Xe concentrates in front of the membrane in the high-pressure compartment (HPC). Method for decrease of low-permeable component (Xe) concentrating

in front of the membrane (HPC) due to the conversion of low-permeable component (Xe) in the gas hydrate phase is proposed. Methane (CH_4) also is low-permeable component. However, at the gas hydrate temperature is 273.15 K CH_4 the gas hydrate dissociation pressure is 2624.52 kPa, which is an order of magnitude greater than Xe the gas hydrate dissociation pressure is 154.30 kPa. Consequently, CH_4 has the worst gas hydrate-forming properties in comparison with Xe. Thus, CH_4 will concentrate in gas phase and Xe will concentrate in the gas hydrate phase.

Theoretical modeling of the hybrid membrane-gas hydrate crystallisation from model binary gas mixtures approximated to natural gas composition and normalised by 100% is considered for improve Xe recovery. The first gas mixture is CO_2 (97.09 vol.%) and Xe (2.91 vol.%). The second gas mixture is H_2S (97.09 vol.%) and Xe (2.91 vol.%). The third gas mixture is CH_4 (99.84 vol.%) and Xe (0.16 vol.%). The process at the gas hydrate mixture dissociation pressures and the gas hydrate formation temperature is 275.15 K. For hydrocarbon systems separation the most widespread industrial the elastomeric membranes: Poly(dimethylsiloxane) (PDMS) and Cellulose triacetate (CTA) [18] are used. They are high permeabilities for acid gases (H_2S , CO_2) and poorly permeabilities for gases under consideration (CH_4 , Xe).

2. Materials and methods

For the gas hydrate formation requires the following three conditions:

- 1) the gas hydrate-forming must not chemically interact with the water;
- 2) gas molecule diameter must be less than the gas hydrate cavity diameter;
- 3) gas pressure in the system must be greater than the gas hydrate dissociation pressure (P_{dis}). The gas hydrate dissociation pressure is the minimum pressure at which the gas hydrate formation process is possible.

If there is gas mixture then a mixed gas hydrate is formed. During the mixed gas hydrate formation gas molecules are redistributed between the gas hydrate and gas mixture phases. In the gas hydrate cavities gas molecules distribution is characterised by the gas hydrate distribution coefficient (α_1) [19]. As a result of the hybrid membrane-gas hydrate crystallisation part of the initial gas mixture the gas hydrates forms with the gas hydrate distribution coefficient $\alpha_1 > 1$ and other gas mixture part permeates through the membrane with the gas hydrate distribution coefficient $\alpha_1 < 1$.

For separation or purification of gas mixture with close the gas hydrate dissociation pressures and different permeabilities through the membrane it is possible to use the membrane gas separation. The application of this method is based on the fact that high-permeable components are concentrated in the low-pressure compartment (LPC) – at the membrane outlet. The ratio of permeabilities through the membrane of the impurity gas (B) to the main gas (A) is characterised by the membrane selectivity (α_2). When $\alpha_2 > 1$ the impurity is concentrated at the membrane outlet in LPC, when $\alpha_2 < 1$ the impurity is concentrated at the membrane inlet in HPC.

For B impurity component the hybrid membrane-gas hydrate coefficient ($\alpha_{1,2}^B$) can be written as:

$$\alpha_{1,2}^B = \frac{y_{1,2}^B (1 - y^B)}{y^B (1 - y_{1,2}^B)}, \quad (1)$$

where y_1^B is B component concentration in the gas hydrate phase, y_2^B is B component concentration in LPC, y^B is B component concentration in HPC.

Material balance scheme of the hybrid membrane-gas hydrate crystallisation is represented in figure 1.

Material balance equation of the hybrid membrane-gas hydrate crystallisation is:

$$N_0 dy^B = y_o^B d(N_1 + N_2) - y_1^B dN_1 - y_2^B dN_2, \quad (2)$$

where N_0 is the initial substance quantity in HPC, y_o^B is the initial B component concentration in gas mixture, N_1 is the substance quantity with gas concentration contained in the gas hydrate phase, N_2 is the substance quantity with gas concentration in LPC.

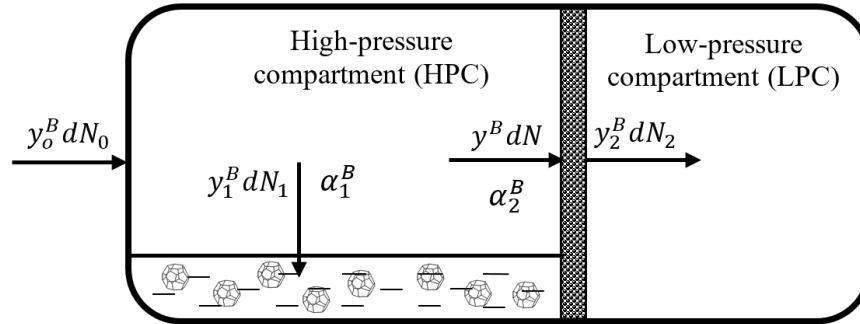


Figure 1. Material balance scheme of the hybrid membrane-gas hydrate crystallisation.

By substituting Eq. (1) into Eq. (2) and after adding a parameter p , which characterises the ratio of the substance amount with gas concentration in LPC to the substance amount with gas concentration contained in the gas hydrate phase ($p=N_2/N_1$), we obtain:

$$N_0 dy^B = y_o^B (1 + p) dN_1 - \left(\frac{\alpha_1^B y^B}{1 + (\alpha_1^B - 1) y^B} + \frac{\alpha_2^B y^B}{1 + (\alpha_2^B - 1) y^B} \right) dN_1 \quad (3)$$

When binary gas mixtures are considered in the case when B impurity component concentration is larger than 10^{-4} vol.%, Eq. (3) can be solved using the numerical method:

$$N_0 dy^B = f(y^B) dN_1, \quad (4)$$

where $f(y^B)$ is the function is describing the change in B impurity concentration in LPC and in the gas hydrate phase relative to the initial B impurity concentration in the hybrid membrane-gas hydrate module.

Eq. (4) is solved under the boundary condition $y = y_o$ at $N_1 = 0$. After integration of Eq. (4) we have:

$$\int_{y_o}^y \frac{dy^B}{f(y^B)} = \frac{N_1}{N_0} = F \quad (5)$$

If B component concentration in the gas hydrate phase is $y_1^B = \alpha_1^B \cdot y^B$, then B component the gas hydrate recovery is defined as:

$$R_{gh} = \frac{y_1^B}{y_o^B} = \frac{\alpha_1^B \cdot y^B}{y_o^B} \quad (6)$$

If B component is withdrawn through the membrane with the concentration is $y_2^B = \alpha_2^B \cdot y^B$, then B component the membrane recovery is expressed as:

$$R_{mem} = \frac{y_2^B}{y_o^B} = \frac{\alpha_2^B \cdot y^B}{y_o^B} \quad (7)$$

In the case of the hybrid crystallisation, B component the membrane-gas hydrate recovery takes the form:

$$R_{hyb} = R_{gh} + R_{mem} = \frac{\alpha_1^B \cdot y^B + \alpha_2^B \cdot y^B}{y_o^B} \quad (8)$$

Also, add the variables that characterise gas mixture withdrawn with the gas hydrate phase (Q_{gh}), gas mixture withdrawn through the membrane (Q_{mem}), and gas mixture withdrawn by the hybrid membrane-gas hydrate crystallisation (Q_{hyb}):

$$Q_{gh} = \frac{N_1}{N_0 + N_1 + N_2} = \frac{F}{(1+p) \cdot F + 1} \quad (9)$$

$$Q_{mem} = \frac{N_2}{N_0 + N_1 + N_2} = \frac{p \cdot F}{(1+p) \cdot F + 1} \quad (10)$$

$$Q_{hyb} = \frac{N_1 + N_2}{N_0 + N_1 + N_2} = \frac{(1+p) \cdot F}{(1+p) \cdot F + 1} \quad (11)$$

As follows from Eqs. (9)-(11) that gas mixture withdrawn is characterised B component concentration degree in HPC or LPC regarding B component concentration in the hybrid membrane-gas hydrate module.

3. Results and discussion

In the hybrid membrane-gas hydrate crystallisation the constant gas hydrate mixture pressure due to the constant input of the initial gas mixture. A vapour pressure of the water (P_w) in the hybrid membrane-gas hydrate module, equal to the saturated vapour pressure of the water, a stable the gas hydrate formation provides. We adopt $P_w = \text{const}$ since there is the constant vapour pressure of the water. The individual gas hydrate dissociation pressures were calculated according to [20]. The calculation results are represented in table 1.

Table 1. Individual gas hydrate dissociation pressures at $T=275.15$ K.

Gas	CH ₄	CO ₂	Xe	H ₂ S
Dissociation pressure, kPa	3117.80	1493.84	183.84	116.64

As shown in table 1, the highest gas hydrate dissociation pressure of gases under consideration has CH₄, the smallest gas hydrate dissociation pressure has H₂S. Consequently, H₂S will adsorb by the gas hydrate cavities in a greater degree.

For theoretical modeling of the hybrid membrane-gas hydrate crystallisation as A basic gases are CH₄, CO₂, H₂S, and as B gas is Xe. Gas hydrate mixture dissociation pressures and Xe gas hydrate distribution coefficients were calculated according to [20]. The calculation results are listed in table 2.

Table 2. Gas hydrate mixture dissociation pressures and Xe gas hydrate distribution coefficients at $T=275.15$ K.

Gas mixture	P_{mix} , kPa	$\alpha_1(\text{Xe})$
CO ₂ =97.09 vol.%, Xe=2.91 vol.%	1238.41	5.95
H ₂ S=97.09 vol.%, Xe=2.91 vol.%	1769.26	0.64
CH ₄ =99.84 vol.%, Xe=0.16 vol.%	3040.57	12.58

Table 2 shows that the highest Xe gas hydrate distribution coefficient in CH₄=99.84 vol.%, Xe=0.16 vol.% gas mixture. This is due to the fact that this gas mixture has the greatest difference in the gas hydrate dissociation pressures, therefore, Xe recovery from the main natural gas component – CH₄ by the gas hydrate crystallisation will effective.

Gas amount permeates through the membrane is characterised by gas permeability through the membrane. Gas permeabilities through PDMS and CTA membrane are represented in table 3.

Table 3. Gas permeabilities through PDMS and CTA membrane.

Membrane type	Gas permeability, Barrer			
	CH ₄	CO ₂	H ₂ S	Xe
PDMS	950.00 [16]	3250.00 [16]	10000.00 [16]	532.00 [17]
CTA	0.25 [21]	7.20 [21]	20.00 [22]	0.11 [23]

According to table 3, industrial the elastomeric membranes are the most permeable for H₂S in comparison with gases under consideration. This result is explained by the highest H₂S solubilities in the elastomeric membranes and high diffusion coefficient relative to gases under consideration. Gas permeabilities decreases in the following order: H₂S > CO₂ > CH₄ > Xe.

The membrane selectivity is the determining parameter in the membrane gas separation. PDMS and CTA membrane selectivities for Xe-based gas mixtures are shown in table 4.

Table 4. PDMS and CTA membrane selectivities for Xe-based gas mixtures.

Membrane type	$\alpha_2(\text{Xe}/\text{CO}_2)$	$\alpha_2(\text{Xe}/\text{H}_2\text{S})$	$\alpha_2(\text{Xe}/\text{CH}_4)$
PDMS	0.16	0.05	0.56
CTA	0.02	0.01	0.44

The membrane selectivity characterises the membrane gas separation efficiency of the recovery gas with regard to the main gas. Consequently, the greater difference in gas permeabilities of the recovery (Xe) and the main (CH_4 , CO_2 , H_2S) gases, the less selectivity and the more effective of the membrane gas separation. Table 4 shows that the greatest difference in gas permeabilities, i.e., the less selectivity has $\text{Xe}/\text{H}_2\text{S}$ gas mixture. PDMS and CTA membrane selectivities for Xe-based gas mixtures decreases in the following order: $\text{Xe}/\text{CH}_4 > \text{Xe}/\text{CO}_2 > \text{Xe}/\text{H}_2\text{S}$. Consequently, Xe/CO_2 and $\text{Xe}/\text{H}_2\text{S}$ gas mixtures have the most efficient membrane gas separation. This is due to the fact that CO_2 and H_2S molecules have the smaller kinetic diameter [24] and the largest diffusion coefficient [25] in comparison with CH_4 and Xe molecules. Thereby, CH_4 and Xe are the poorly soluble in the elastomeric membranes and the considered acid gases (CO_2 , H_2S) are the good soluble in the elastomeric membranes.

Xe recovery from $\text{CO}_2=97.09$ vol.% and $\text{Xe}=2.91$ vol.% gas mixture is considered. This composition is selected from the average ratio of natural gas components and is normalised to 100%. Xe gas hydrate distribution coefficient is $\alpha_1(\text{Xe})=5.95$ at the gas hydrate temperature is $T=275.15$ K and the gas hydrate mixture dissociation pressure is $P_{\text{mix}}=1238.41$ kPa. For PDMS membrane $\alpha_2(\text{Xe}/\text{CO}_2)$ is 0.16 and for CTA membrane $\alpha_2(\text{Xe}/\text{CO}_2)$ is 0.02. The dependences of the gas hydrate, the membrane, and the hybrid membrane-gas hydrate Xe recoveries through PDMS and CTA membranes versus gas mixture withdrawn with the gas hydrate, through the membrane, and by the hybrid membrane-gas hydrate crystallisation at $p=10$ and $p=20$ for $\text{CO}_2=97.09$ vol.% and $\text{Xe}=2.91$ vol.% gas mixture are shown in figure 2.

Figure 2(a) shows that at gas mixture withdrawn with the gas hydrate increases, Xe gas hydrate recovery increases. This is due to the fact that when Xe concentration in the gas hydrate phase of HPC (y_1^{Xe}) increases, Xe concentration in gas phase of HPC (y^{Xe}) decreases, consequently, Xe gas hydrate recovery increases. Gases with the low gas hydrate dissociation pressures and the low gas permeabilities through the membrane will the more efficiently concentrated in the gas hydrate phase of HPC.

At gas mixture withdrawn with the gas hydrate is $Q_{gh}=0.35$ Xe gas hydrate recovery through CTA membrane at $p=20$ is 8.13 (figure 2(a)). At gas mixture withdrawn through the membrane is $Q_{mem}=0.35$ Xe membrane recovery through CTA membrane at $p=20$ is 0.03 (figure 2(b)). This is due to the fact that in $\text{CO}_2=97.09$ vol.% and $\text{Xe}=2.91$ vol.% gas mixture Xe has an order of magnitude less the gas hydrate dissociation pressure (table 2) and an order of magnitude less permeability through PDMS and CTA membrane (table 3) in comparison with CO_2 . Therefore, Xe is the good gas hydrate-forming and will concentrate in the gas hydrate phase of HPC. CO_2 is the highly permeable through the membrane and the poorly gas hydrate-forming, therefore, CO_2 will permeate through the membrane and will concentrate in LPC.

The greater difference between the permeability of gases under consideration, the more efficient is low-permeable component recovery by the hybrid membrane-gas hydrate crystallisation. The lower membrane permeability, the more efficient Xe is concentrated in the gas hydrate phase. Consequently, Xe gas hydrate recovery is more effective when using CTA membrane.

It can be seen from figure 2(a) that with p increasing, i.e., with an increase in the ratio of the substance amount with gas concentration in LPC to the substance amount with gas concentration contained in the gas hydrate phase, Xe gas hydrate recovery increases. The higher CO_2 concentration in LPC at the constant Xe concentration in the gas hydrate phase, the higher p . With p increasing from 10 to 20 Xe gas hydrate recovery for PDMS and CTA membranes increases in 1.10 times. Xe gas

hydrate recovery for CTA membrane in 1.04 times more than for PDMS membrane. Consequently, Xe gas hydrate recovery is more dependent versus p than versus the membrane type.

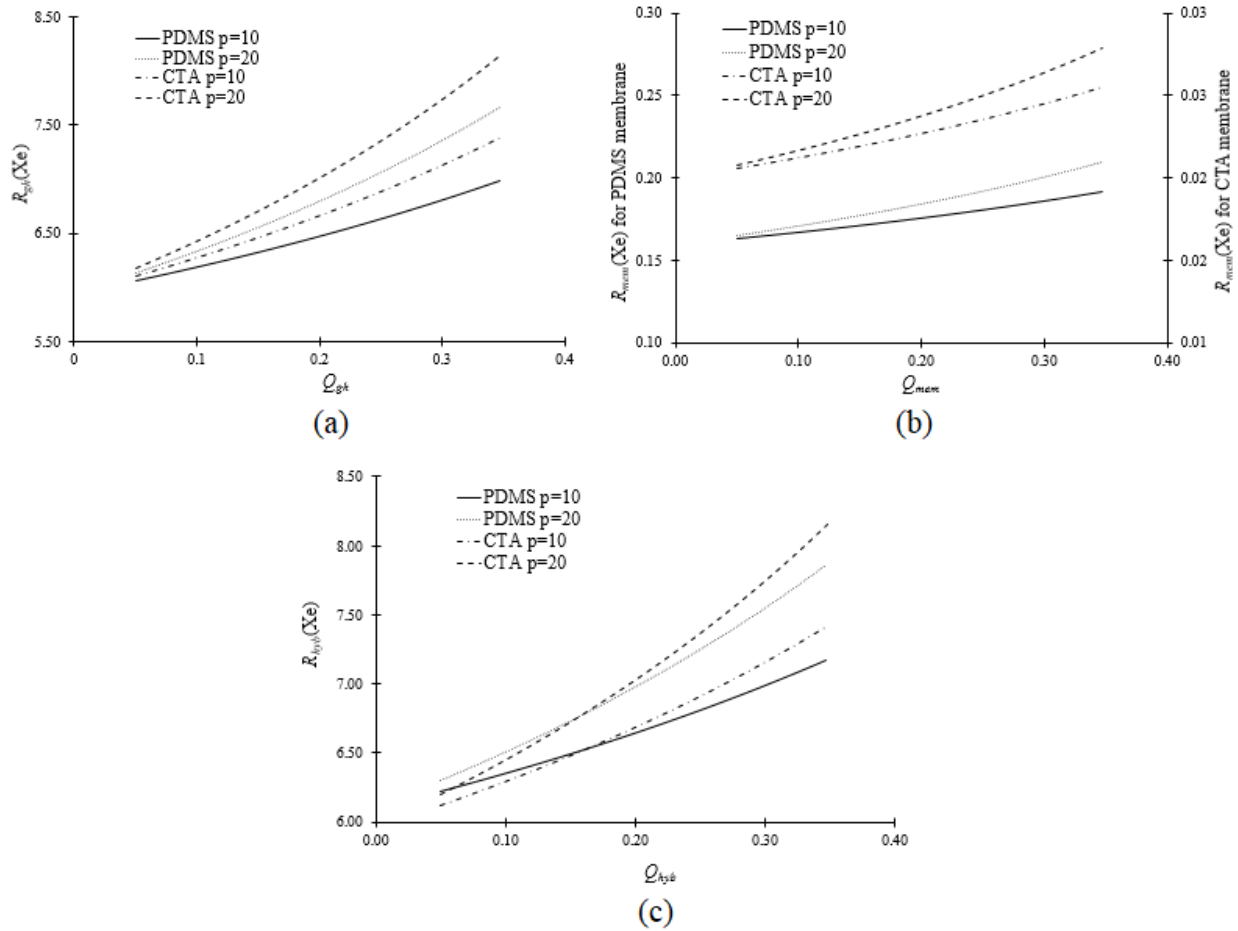


Figure 2. The dependences of Xe gas hydrate (a), Xe membrane (b), and Xe membrane-gas hydrate (c) recoveries through PDMS and CTA membranes versus gas mixture withdrawn with the gas hydrate (a), through the membrane (b), and by the hybrid membrane-gas hydrate crystallisation (c) at $p=10$ and $p=20$ for $CO_2=97.09$ vol.% and $Xe=2.91$ vol.% gas mixture.

As follows from figure 2(b), Xe membrane recovery for PDMS membrane is eight times greater than for CTA membrane. This is due to the fact that PDMS membrane in compared with CTA membrane have the greater substituents number in the polymer chain, the more free volume, hence, have the greater permeability.

Figures 2(c) depicts that Xe membrane-gas hydrate recovery the most effective when CTA membrane is used. This is due to the fact that Xe is the gas hydrate-forming and for Xe concentration increase in the gas hydrate phase it is necessary the membranes with the low permeability for Xe and the high permeability for other gases are used. With gas mixture withdrawn by the hybrid membrane-gas hydrate crystallisation (Q_{hyb}) increased from 0.05 to 0.35 Xe membrane-gas hydrate recovery on average increases by 1.23 times. It is also shown that Xe membrane-gas hydrate recovery $R_{hyb}(Xe)$ is 1.37 times higher than the conventional gas hydrate crystallisation. Xe membrane-gas hydrate recovery at gas mixture withdrawn by the hybrid membrane-gas hydrate crystallisation Q_{hyb} is 0.35 for CTA membrane at $p=20$.

Also, Xe recovery is considered from $H_2S=97.09$ vol.% and $Xe=2.91$ vol.% gas mixture. This composition is selected from the average ratio of natural gas components and is normalised to 100%. Xe gas hydrate distribution coefficient is $\alpha_1(Xe)=0.64$ at the gas hydrate temperature is $T=275.15$ K and the gas hydrate mixture dissociation pressure is $P_{mix}=1769.26$ kPa. For PDMS membrane $\alpha_2(Xe/H_2S)$ is 0.05 and for CTA membrane $\alpha_2(Xe/H_2S)$ is 0.01. The dependences of the gas hydrate, the membrane, and the membrane-gas hydrate Xe recoveries through PDMS and CTA membranes versus gas mixture withdrawn with the gas hydrate, through the membrane, and by the hybrid membrane-gas hydrate crystallisation at $p=10$ and $p=20$ for $H_2S=97.09$ vol.% and $Xe=2.91$ vol.% gas mixture are shown in figure 3.

As can be seen from figure 3(a), Xe gas hydrate recovery increases with gas mixture withdrawn with the gas hydrate increasing and the weak depending versus the membrane type and p . In $H_2S=97.09$ vol.% and $Xe=2.91$ vol.% gas mixture H_2S has the less the gas hydrate dissociation pressure in comparison with Xe (table 2). Therefore, H_2S is the best gas hydrate-forming in comparison with Xe. However, H_2S permeabilities through PDMS and CTA membrane are two orders of magnitude greater than Xe permeabilities (table 3). Consequently, H_2S will concentrate in the gas hydrate phase and also permeate through the membrane in LPC. Figures 3(a),(b) shows that Xe gas hydrate recovery is twelve times more effective than Xe membrane recovery.

Figures 3(a)-(c) depicts that in $H_2S=97.09$ vol.% and $Xe=2.91$ vol.% gas mixture Xe membrane-gas hydrate recovery is eight times less than in $CO_2=97.09$ vol.% and $Xe=2.91$ vol.% gas mixture (figures 2(a)-(c)). This is due to the fact that H_2S has the better gas hydrate-forming properties in comparison with CO_2 . Therefore, for the most efficient Xe recovery from natural gas it is necessary to remove impurities with the gas hydrate dissociation pressures close to Xe.

As follows from figure 3(b), Xe membrane recovery for PDMS membrane is five times more efficient than for CTA membrane. This is due to the fact that Xe permeability through PDMS membrane is three orders of magnitude greater than Xe permeability through CTA membrane (table 3). For Xe recovery by the hybrid membrane-gas hydrate crystallisation from $H_2S=97.09$ vol.% and $Xe=2.91$ vol.% gas mixture PDMS membrane is more effectively (figure 3(c)). Xe membrane-gas hydrate recovery for PDMS membrane is 1.04 times greater than for CTA membrane. It is shown that Xe membrane-gas hydrate recovery $R_{hyb}(Xe)$ is 1.59 times higher than the conventional gas hydrate crystallisation. Xe membrane-gas hydrate recovery at gas mixture withdrawn by the hybrid membrane-gas hydrate crystallisation is $Q_{hyb}=0.35$ for PDMS membrane at $p=20$.

The third model gas mixture is $CH_4=99.84$ vol.% and $Xe=0.16$ vol.%. This composition is selected from the average ratio of natural gas components and is normalised to 100%. Xe gas hydrate distribution coefficient is $\alpha_1(Xe)=12.58$ at the gas hydrate temperature is $T=275.15$ K and the gas hydrate mixture dissociation pressure is $P_{mix}=3040.57$ kPa. For PDMS membrane $\alpha_2(Xe/CH_4)$ is 0.56 and for CTA membrane $\alpha_2(Xe/CH_4)$ is 0.44. The dependences of the gas hydrate, the membrane, and the membrane-gas hydrate Xe recoveries through PDMS and CTA membranes versus gas mixture withdrawn with the gas hydrate, through the membrane, and by the hybrid membrane-gas hydrate crystallisation at $p=10$ and $p=20$ for $CH_4=99.84$ vol.% and $Xe=0.16$ vol.% gas mixture are shown in figure 4.

It can be seen from figure 4(a) that when gas mixture withdrawn with the gas hydrate (Q_{gh}) increasing, Xe gas hydrate recovery increases. Xe has the better gas hydrate-forming properties in comparison with CH_4 , as Xe gas hydrate dissociation pressure the order of magnitude less than CH_4 gas hydrate dissociation pressure (table 1). Consequently, Xe will concentrate in the gas hydrate phase. Since CH_4 and Xe permeabilities are close (table 3), consequently, CH_4 will concentrate in gas phase of HPC. As can be seen from figures 4(a),(b) that Xe gas hydrate recovery is 20.64 times more effective in comparison with Xe membrane recovery.

As can be seen from figure 4(a) that with p increasing, Xe gas hydrate recovery decreases. This is due to the fact that when in the gas hydrate phase Xe concentration increasing at the constant gas concentration in LPC, the ratio p of gas concentration in LPC to gas concentration in the gas hydrate

phase decreases. Figures 4(a)-(c) shows that the most efficient Xe recovery when PDMS membrane is used.

At gas mixture withdrawn by the hybrid membrane-gas hydrate crystallisation is $Q_{hyb}=0.35$ Xe gas hydrate-membrane recovery is 20.08. It is also shown that Xe membrane-gas hydrate recovery $R_{hyb}(Xe)$ is 1.60 times higher than the conventional gas hydrate crystallisation. Xe membrane-gas hydrate recovery at gas mixture withdrawn by the membrane-gas hydrate crystallisation is $Q_{hyb}=0.35$ for PDMS membrane at $p=10$. Thus, the efficiently Xe recovery from the main natural gas component – CH_4 by the hybrid membrane-gas hydrate crystallisation is possible.

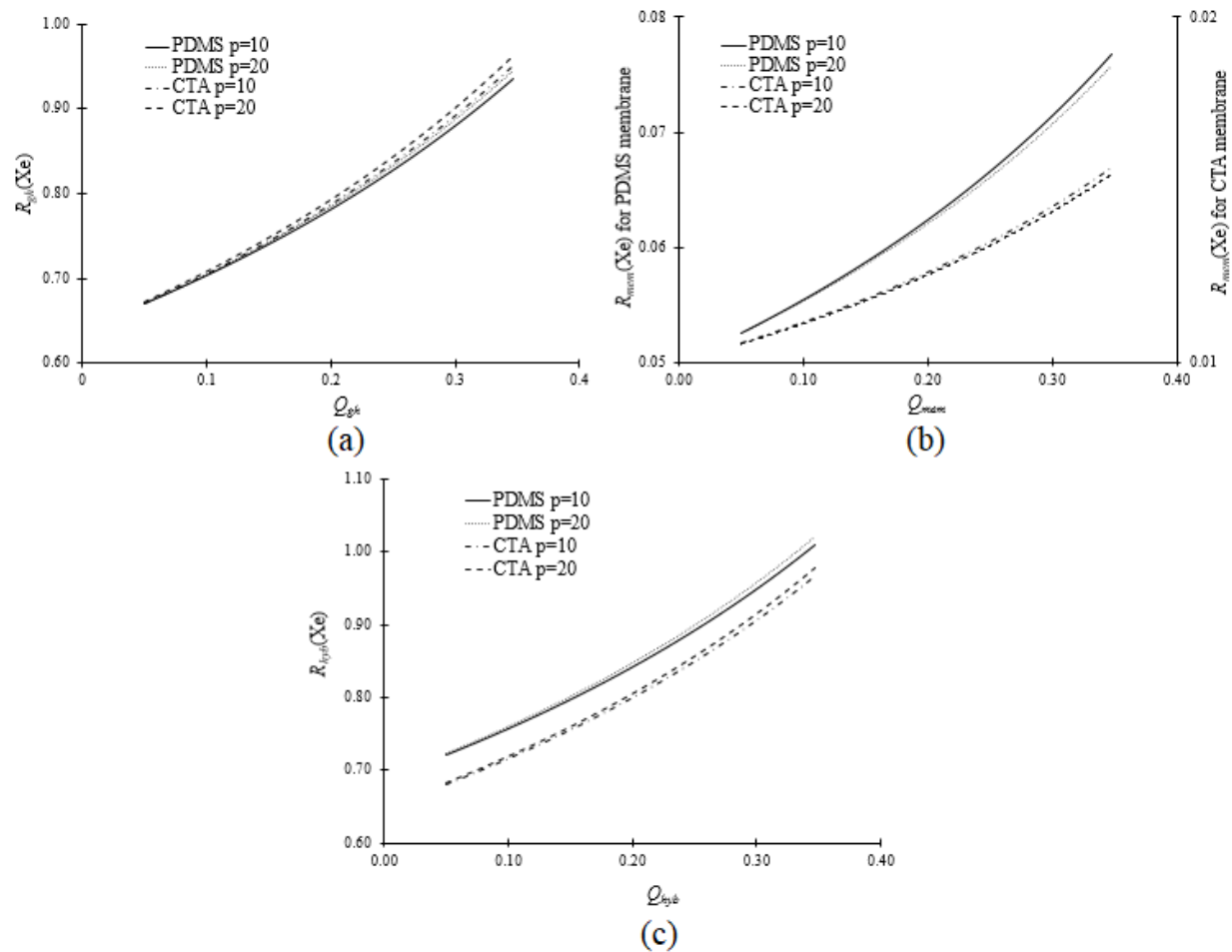


Figure 3. The dependences of Xe gas hydrate (a), Xe membrane (b), and Xe membrane-gas hydrate (c) recoveries through PDMS and CTA membranes versus gas mixture withdrawn with the gas hydrate (a), through the membrane (b), and by the hybrid membrane-gas hydrate crystallisation (c) at $p=10$ and $p=20$ for $H_2S=97.09$ vol.% and $Xe=2.91$ vol.% gas mixture.

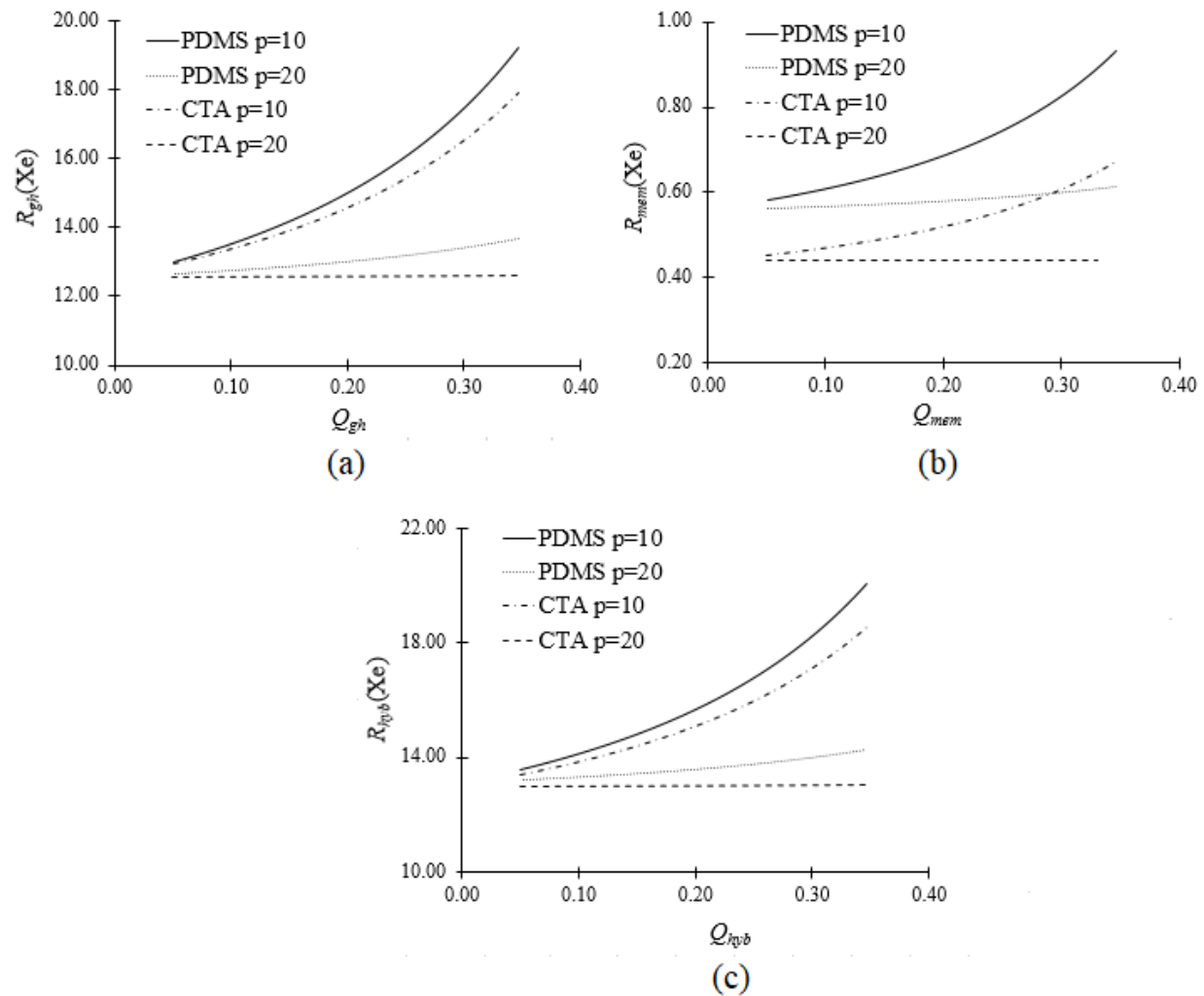


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4. Conclusion

Based on the mathematical model of the membrane-gas hydrate crystallisation the efficiency of Xe recovery from binary gas mixtures approximated to natural gas composition is considered. It is found that the largest Xe recovery is 20.08 in $CH_4=99.84$ vol.% and $Xe=0.16$ vol.% gas mixture at gas mixture withdrawn by the hybrid membrane-gas hydrate crystallisation is $Q_{hyb}=0.35$. It is established that the greatest impurity component recovery can be achieved for binary gas mixtures in which one gas has the low gas hydrate dissociation pressure and the low permeability through the membrane, and the second gas has the high gas hydrate dissociation pressure and the high permeability through the membrane. In the membrane-gas hydrate crystallisation hydrocarbons removal (for example, CH_4) from HPC from natural gas is necessary for Xe recovery increase. It is shown that the use of the hybrid membrane-gas hydrate crystallisation allows the more effective Xe recovery both from acid gases and from hydrocarbons in comparison with the conventional gas hydrate crystallisation.

Acknowledgments

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